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Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy

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Abstract

The generation of energy by clean, efficient and environmental-friendly means is now one of the major challenges for engineers and scientists. Fuel cells convert chemical energy of a fuel gas directly into electrical work, and are efficient and environmentally clean, since no combustion is required. Moreover, fuel cells have the potential for development to a sufficient size for applications for commercial electricity generation. This paper outlines the acute global population growth and the growing need and use of energy and its consequent environmental impacts. The existing or emerging fuel cells' technologies are comprehensively discussed in this paper. In particular, attention is given to the design and operation of Solid Oxide Fuel Cells (SOFCs), noting the restrictions based on materials' requirements and fuel specifications. Moreover, advantages of SOFCs with respect to the other fuel cell technologies are identified. This paper also reviews the limitations and the benefits of SOFCs in relationship with energy, environment and sustainable development. Few potential applications, as long-term potential actions for sustainable development, and the future of such devices are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Energy; Environment; Solid Electrolytes; Electrodes

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1. Introduction

Today fuel cells are much in the news since they appear to be one of the most efficient and effective solutions to environmental problems that we face today. It is now well established that global warming is taking place due to effluent gas emission, mainly CO_2. During the past century, global surface temperatures have increased at a rate near 0.6°C/century [1]. This trend has dramatically increased during the past 25 years: the temperature rise is 2.3, 1.3 and 1.7°C according to the three well-known centres assessing this phenomenon i.e., Princeton in the USA, Hamburg in Germany, and IPCC of London in the U.K. Moreover, according to the US National Oceanic and Atmospheric Administration and the Scripps Institute of Oceanography in San Francisco, the average temperature of the Atlantic, Pacific and Indian Oceans (covering 72% of the earth's surface) has risen by 0.06°C since 1995. Global temperatures in 2001 were 0.52°C above the long-term 1880–2000 average (*the 1880–2000 annually averaged combined land and ocean temperature is 13.9°C*). Also, according to the US Department of Energy (DoE), world emissions of carbon are expected to increase by 54% above 1990 levels by 2015 making the earth likely to warm 1.7–4.9°C over the period 1990–2100, as shown in Fig. 1 [2]. Tables 1, 2 and 3 show respectively the total CO_2 emissions of the top 15 nations, the CO_2 emissions of top industrial nations per capita and by unit Gross National Product (GNP) [3].

Problems with energy supply and use are related not only to global warming but also to such environmental concerns as air pollution, acid precipitation, ozone depletion, forest destruction, and emission of radioactive substances.

World population keeps increasing at 1.2–2% per year, so that it is expected to reach 12 billions in 2050. Therefore, economic development will almost certainly continue to grow. Global demand for energy services is expected to increase by as much as an order of magnitude by 2050, while primary-energy demands are expected to increase by 1.5 to 3 times [4], as seen in Table 4. As worldwide oil supplies

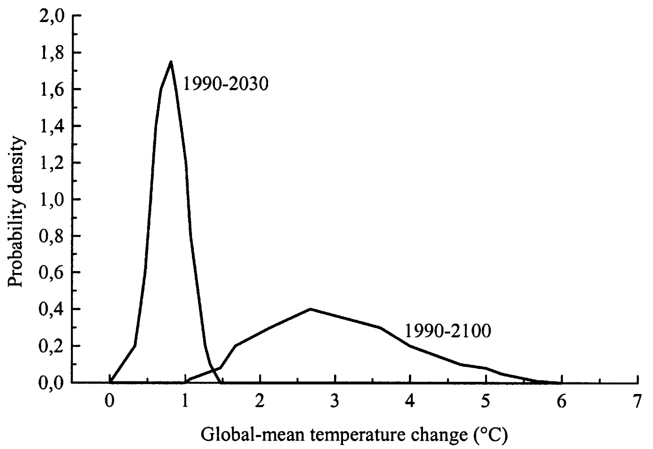


Fig. 1. Global–mean temperature change over the period of 1990–2100 and 1990–2030.

Table 1
Global emissions of the top 15 nations by total CO_2 volume (billions of tonnes)

Rank	Nation	CO_2	Rank	Nation	CO_2	Rank	Nation	CO_2
1	USA	1.36	6	India	0.19	11	Mexico	0.09
2	Russia	0.98	7	UK	0.16	12	Poland	0.08
3	China	0.69	8	Canada	0.11	13	S. Africa	0.08
4	Japan	0.30	9	Italy	0.11	14	S. Korea	0.07
5	Germany	0.27	10	France	0.10	15	Australia	0.07

Table 2
Global emissions of the top fifteen CO_2 producing nations per capita (tonnes)

Rank	Nation	CO_2	Rank	Nation	CO_2	Rank	Nation	CO_2
1	USA	19.1	6	UK	10.1	11	France	6.3
2	Russia	18.0	7	Japan	8.8	12	S. Korea	5.8
3	Australia	14.4	8	Poland	7.7	13	Mexico	3.6
4	Canada	13.9	9	Italy	7.1	14	China	2.1
5	Germany	12.2	10	S. Africa	7.1	15	India	0.8

Table 3
Global emissions of the top industrial nations producing CO_2 per unit GNP (Gross National Product)

Rank	Nation	CO_2	Rank	Nation	CO_2	Rank	Nation	CO_2
1	Russia	7591	4	Canada	708	7	Italy	366
2	China	4015	5	UK	549	8	Japan	271
3	USA	740	6	Germany	477	9	France	255

Table 4
Population, energy and electricity demands ([a]Millions of Barrels per Day of Oil Equivalent

Year	Population (billions)	Energy demand, MBDOE[a])	Electricity demand, % Energy demand
1940	2.4	70	–
1960	3.0	90	–
1970	3.6	100	6
1985	4.8	200	12
1995	5.3	300	15
2000	6.1	350	30
2001	7.2	410	50

dwindle (Fig. 2 [5]), the development of new power generation technologies will become increasingly important. Simultaneously, interest will likely increase regarding energy-related environmental concerns. Indeed, energy is one of the main factors that must be considered in discussions of sustainable development. In response to the critical need for a cleaner energy technology, some potential solutions have evolved, including energy conservation through improved energy efficiency, reduction in the consumption of fossil fuels, and an increase in the supply of environmental-friendly energy, such as renewable sources and fuel cells. Electricity from fuel cells can be used in the same way as grid power. One such technology is the solid oxide fuel cell (SOFC), which is one of the most efficient and environmental-friendly technologies available for generating power from hydrogen, natural gas, and other renewable fuels. Large-scale, utility-based SOFC power generation systems have reached pilot-scale demonstration stages in the US, Europe, and in Japan. Small-scale SOFC systems are being developed for military, residential, industrial, and transportation applications.

2. Fuel cells

A fuel cell is an energy conversion device that converts the chemical energy of a fuel gas directly to electrical energy and heat without the need for direct combustion as an intermediate step, giving much higher conversion efficiencies than conventional thermomechanical methods. The operating principles of fuel cells are similar to those of batteries, i.e., electrochemical combination of reactants to generate electricity, a combination made of a gaseous fuel (hydrogen) and an oxidant gas (oxygen from the air) through electrodes and via an ion conducting electrolyte. However, unlike a battery, a fuel cell does not run down or require recharging. A fuel cell operates as long as both fuel and oxidant are supplied to the electrodes and the influence it exerts on the surrounding environment is negligible.

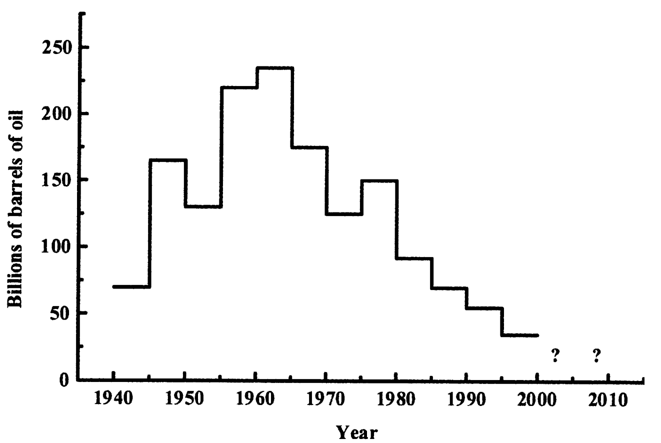


Fig. 2. Volume of oil discovered world wide every five years.

2.1. Fuel cell origins

Despite their modern high-tech aura, fuel cells actually have been known to science for more than 160 years and have become the subject of intense research and development, especially since World War II. Alessandro Volta (1745–1827) was the first scientist to place the observations of the electrical phenomena on a scientific footing. J. W. Ritter (1776–1810), also known as the founder of the electrochemistry, has continued to develop the understanding of electricity. Sir Humphrey Davy created, in 1802, a simple fuel cell based upon a compound (C/H_2O, $NH_3/O_2/C$) delivering a feeble electric shock. The discovery of the principle of the fuel cell is due to Christan Friedrich Schönbein from 1829 to 1868. Sir William Grove (1811–1896), an English lawyer turned scientist, won renown for his development of an improved wet-cell battery in 1838, the 'Grove cell', as it came to be called. This cell type is based on reversing the electrolysis of water [6]. Ceramic fuel cells came much later and began with Nernst's discovery of solid oxide electrolytes in 1899 [7]. Ludwig Mond (1839–1909) spent most of his career developing industrial chemical technology. Mond and assistant Carl Langer (d. 1935) described their experiments with a hydrogen–oxygen fuel cell that attained 6 amps per square foot (measuring the surface area of the electrode) at 0.73 V. Friedrich Wilhelm Ostwald (1853–1932), a founder of the field of physical chemistry, provided much of the theoretical understanding of how fuel cells operate. Emil Baur (1873–1944) of Switzerland conducted wide-ranging research into different types of fuel cells during the first half of the 20th century. Baur's work included high temperature devices (using molten silver as an electrolyte) and a unit that used a solid electrolyte of clay and metal oxides. Francis Thomas Bacon (1904–1992) began researching alkali electrolyte fuel cells in the late 1930s. In 1939, his first cell was built. Since 1945, three research groups (US, Germany and the former USSR) took over the studies on some principal types of generators by improving their technologies for industrial development purposes. These works yielded the actual concepts, namely at Siemens, and Pratt & Wittney [8]. In connection with the space program Apollo in 1960, NASA spent tens of millions of dollars in a successful program that used hydrogen-based fuel cells to power the on-board electrical systems on the Apollo journey to the moon.

Beginning in the mid-1980s government agencies in the US, Canada and Japan significantly increased their funding for fuel cell R&D.

Today, fuel cells are common in spaceflight (Space Shuttle, Skylab and Gemini spacecrafts), transportation and make sense for use as portable power, home power generation and large power generation.

2.2. Types of fuel cells

Fuel cells are generally classified by the chemical characteristics of the electrolyte used as the ionic conductor in the cell, as summarised in Table 5. The first five types are characterised by their low to medium temperature of operation (50–210°C), their relatively low electrical generation efficiencies (40–50% when operated on readily available fuels such as methanol and hydrocarbons, 50% when using pure hydrogen

Table 5
Technical characteristics of different fuel cells

Types of fuel cell	Electrolyte	Operating T	Fuel	Oxidant	Efficiency
Alkaline (AFC)	potassium hydroxide (KOH)	50–200°C	pure hydrogen, or hydrazine	O_2/Air	50–55%
Direct methanol (DMFC)	polymer	60–200°C	liquid methanol	O_2/Air	40–55%
Phosphoric acid (PAFC)	phosphoric acid	160–210°C	hydrogen from hydrocarbons and alcohol	O_2/Air	40–50%
Sulfuric acid (SAFC)	sulfuric acid	80–90°C	alcohol or impure hydrogen	O_2/Air	40–50%
Proton-exchange membrane (PEMFC)	polymer, proton exchange membrane	50–80°C	less pure hydrogen from hydrocarbons or methanol	O_2/Air	40–50%
Molten carbonate(MCFC)	molten salt such as nitrate, sulphate, carbonates…	630–650°C	hydrogen, carbon monoxide, natural gas, propane, marine diesel	CO_2/O_2/Air	50–60%
Solid oxide (SOFC)	ceramic as stabilised zirconia and doped perovskite	600–1000°C	natural gas or propane	O_2/Air	45–60%
Protonic ceramic (PCFC)	thin membrane of barium cerium oxide	600–700°C	hydrocarbons	O_2/Air	45–60%

fuel). The latter three types are characterised by their high temperature of operation (600–1000°C), their ability to utilise methane directly in the fuel cell and thus their high inherent generation efficiency (45–60% for common fuels such as natural gas, 90% with heat recovery) [9]. There are also other types of fuel cells which are less employed, but may later find a specific application. Examples are the air-depolarised cells, sodium amalgam cells, biochemical fuel cells, inorganic redox cells, regenerative cells, alkali metal–halogen cells, etc.

Present materials' science has made the fuel cells a reality in some specialised applications. By far the greatest research interest throughout the world has focussed on Proton Exchange Membrane (PEM) and Solid Oxide (SO) cell stacks. PEMs are well advanced type of fuel cell that are suitable for cars and mass transportation. SOFC technology is the most demanding from a materials standpoint and is developed for its potential market competitiveness arising from:

- SOFCs are the most efficient (fuel input to electricity output) fuel cell electricity generators currently being developed world-wide.
- SOFCs are flexible in the choice of fuel such as carbon-based fuels, eg, natural gas.
- SOFC technology is most suited to applications in the distributed generation (ie, stationary power) market because its high conversion efficiency provides the greatest benefit when fuel costs are higher, due to long fuel delivery systems to customer premises.
- SOFCs have a modular and solid state construction and do not present any moving parts, thereby are quiet enough to be installed indoors.
- The high operating temperature of SOFCs produces high quality heat byproduct which can be used for co-generation, or for use in combined cycle applications.
- SOFCs do not contain noble metals that could be problematic in resource availability and price issue in high volume manufacture.
- SOFCs do not have problems with electrolyte management (liquid electrolytes, for example, which are corrosive and difficult to handle).
- SOFCs have extremely low emissions by eliminating the danger of carbon monoxide in exhaust gases, as any CO produced is converted to CO_2 at the high operating temperature.
- SOFCs have a potential long life expectancy of more than 40000–80000 h.

3. Solid oxide fuel cells

SOFCs have recently emerged as a serious high temperature fuel cell technology. They promise to be extremely useful in large, high-power applications such as full-scale industrial stations and large-scale electricity-generating stations. Some fuel cell developers see SOFCs being used in motor vehicles. A SOFC system usually utilizes a solid ceramic as the electrolyte and operates at extremely high temperatures (600–1000°C). This high operating temperature allows internal reforming, promotes rapid electrocatalysis with non-precious metals, and produces high quality byproduct heat

for co-generation. Efficiencies for this type of fuel cell can reach up to 70% with an additional 20% as heat recovery. SOFCs are best suited for provision of power in utility applications due to the significant time required to reach operating temperatures.

3.1. Solid oxide fuel cell history

Emil Baur, a Swiss scientist and his colleague H. Preis experimented with solid oxide electrolytes in the late 1930s, using such materials as zirconium, yttrium, cerium, lanthanum, and tungsten oxide. The operation of the first ceramic fuel cell at 1000°C, by Baur and Preis, was achieved in 1937 [10]. In the 1940s, O. K. Davtyan of Russia added monazite sand to a mix of sodium carbonate, tungsten trioxide, and soda glass, in order to increase the conductivity and mechanical strength. Davtyan's design, however, also experienced unwanted chemical reactions and short life ratings. By the late 1950s, research into solid oxide technology began to accelerate at the Central Technical Institute in the Hague, Netherlands, Consolidation Coal Company, in Pennsylvania, and General Electric, in Schenectady, New York. A 1959 discussion of fuel cells noted that problems with solid electrolytes included relatively high internal electrical resistance, melting, and short-circuiting, due to semiconductivity. Not everybody gave up on solid oxides, however. The promise of a high-temperature cell that would be tolerant of carbon monoxide and use a stable solid electrolyte continued to draw modest attention. Researchers at Westinghouse, for example, experimented with a cell using zirconium oxide and calcium oxide in 1962. More recently, climbing energy prices and advances in materials technology have reinvigorated work on SOFCs, and a recent report noted about 40 companies working on these fuel cells that include Global Thermoelectric's Fuel Cell Division, which is developing cells designed at the Julich Research Institute in Germany. Cermatec-Advanced Ionic Technologies is working on units up to 10 kW in capacity, running on diesel fuel, which would be used for mobile power generation. The US Department of Energy announced that a SOFC-microturbine co-generation unit has been evaluated, since April 2000, by the National Fuel Cell Research Center and Southern California Edison. The fuel cell was built by Siemens Westinghouse and the microturbine by Northern Research and Engineering Corporation. In a year of actual operating conditions, the 220 kW SOFC, running on natural gas is achieving an efficiency of 60%. Also, a world record for SOFC operation, roughly eight years, still stands, and the prototype cells have demonstrated two critical successes: the ability to withstand more than 100 thermal cycles, and voltage degradation of less than 0.1% per thousand h. Moreover, a 140 kW peak power SOFC cogeneration system, supplied by Siemens Westinghouse, is presently operating in the Netherlands. This system has operated for over 16,600 h, becoming the longest running fuel cell in the world [11]. The first demonstration of the commercial prototype cells in a full scale SOFC module is equally significant.

Partners in a technology development program, DoE and Siemens Westinghouse hope to place a 1 MW fuel cell co-generation plant in operation within this year [12].

3.2. Design and operation of SOFCs

SOFCs differ in many respects from other fuel cell technologies. First, they are composed of all-solid-state materials. Second, the cells can operate at temperatures as high as 1000°C, significantly hotter than any other major category of fuel cell. Third, the solid state character of all SOFC components means that there is no fundamental restriction on the cell configuration. Cells are being constructed in two main configurations, i.e., tubular cells or rolled tubes, such as those being developed at Westinghouse Electric Corporation since the late 1950s, and a flat-plates configuration adopted more recently by many other developers and employed today by the electronics industry.

A SOFC consists of two electrodes sandwiched around a hard ceramic electrolyte such as the remarkable ceramic material called zirconia.

Hydrogen fuel is fed into the anode of the fuel cell and oxygen, from the air, enters the cell through the cathode. By burning fuel containing hydrogen on one side of the electrolyte, the concentration of oxygen is dramatically reduced. The electrode on this surface will allow oxygen ions to leave the electrolyte and react with the fuel which is oxidised, thereby releasing electrons (e^-). On the other side of the plate, which is exposed to air, an oxygen concentration gradient is created across the electrolyte, which attracts oxygen ions from the air side, or cathode, to the fuel side, or anode. If there is an electrical connection between the cathode and the anode, this allows electrons to flow from the anode to the cathode, where a continuous supply of oxygen ions (O^{2-}) for the electrolyte is maintained, and oxygen ions from cathode to anode, maintaining overall electrical charge balance, thereby generating useful electrical power from the combustion of the fuel. The only byproduct of this process is a pure water molecule (H_2O) and heat, as shown in Fig. 3.

The SOFC reactions include:Anode side:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-, CO + O^{2-} \rightarrow CO_2 + 2e^-, CH_4 + 4O^{2-} \rightarrow 2H_2O + CO_2 + 8e^- \ (\textit{Fuel containing hydrogen})$$

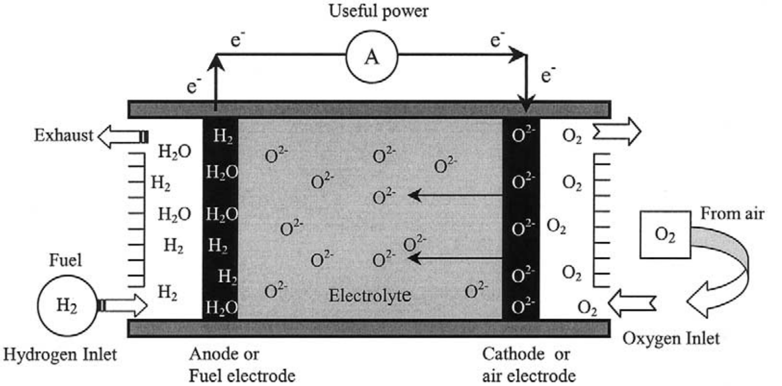


Fig. 3. Concept diagram of SOFC based on oxygen-ion conductors.

Cathode side:

$$O^2 + 4e^- \rightarrow 2O^{2-}$$

Reforming natural gas or other hydrocarbon fuels to extract the necessary hydrogen can be accomplished within the fuel cell, eliminating the need for an external reformer as it is the case for the other types of fuel cells.

3.3. Components of the SOFCs

A SOFC is mainly composed of two electrodes (the anode and the cathode), and a solid electrolyte. The fuel is also important as the principal parameter but independent of the other as it is most of the time converted into hydrogen. The SOFC, which relies on O^{2-} oxygen ion transport, also works with high purity hydrogen, but it does not rely upon this fuel, which is expensive to produce and difficult to handle.

The main function of the electrode is to bring about reaction between the reactant (fuel or oxygen) and the electrolyte, without itself being consumed or corroded. It must also bring into contact the three phases, i.e., the gaseous fuel, the solid electrolyte and the electrode itself.

The anode, used as the negative post of the fuel cell, disperses the hydrogen gas equally over its whole surface and conducts the electrons, that are freed from hydrogen molecule, to be used as a useful power in the external circuit.

The cathode, the positive post of the fuel cell, distributes the oxygen fed to it onto its surface and conducts the electrons back from the external circuit where they can recombine with oxygen ions, passed across the electrolyte, and hydrogen to form water.

The electrolyte determines the operating temperature of the fuel cell and is used to prevent the two electrodes to come into electronic contact by blocking the electrons. It also allows the flow of charged ions from one electrode to the other to maintain the overall electrical charge balance. It can either be an oxygen ion conductor or a hydrogen ion (proton) conductor, the major difference between the two types is the side in the fuel cell in which the water is produced: the oxidant side in proton–conductor fuel cells and the fuel side in oxygen-ion-conductor ones, as shown in Figs. 3 and 4.

3.4. SOFC component requirements

Each component of the SOFC serves several functions and must therefore meet certain requirements such as [13]:

- Proper stability (chemical, phase, morphological, and dimensional)
- Proper conductivity
- Chemical compatibility with other components
- Similar thermal expansion to avoid cracking during the cell operation
- Dense electrolyte to prevent gas mixing
- Porous anode and cathode to allow gas transport to the reaction sites

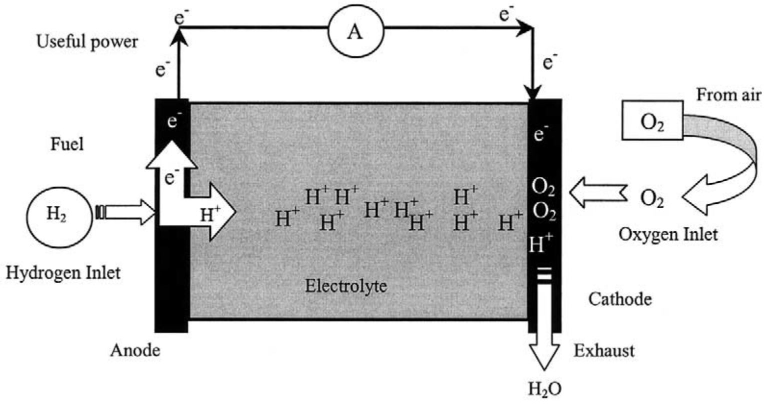


Fig. 4. Concept diagram of SOFC based on proton conductors.

- High strength and toughness properties
- Fabricability
- Amenable to particular fabrication conditions
- Compatibitity at higher temperatures at which the ceramic structures are fabricated
- Low cost

3.5. Materials for cell components

The stability of the following SOFC components materials, over long periods, has been proven by a number of SOFC manufacturers such as the Global Thermoelectric company, Westinghouse Electric Corporation, Siemens (now called Siemens Westinghouse Power Corporation) and Fuji Electric.

3.5.1. Electrolyte

Current technology employs several ceramic materials for the active SOFC components. Although a variety of oxide combinations has been used for solid non-porous electrolytes, the most common to date has been the stabilised zirconia with conductivity based on oxygen ions (O^{2-}), especially yttria-stabilised zirconia (Y_2O_3—stabilised ZrO_2 or YSZ, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ for example) in which a tiny amounts of the element yttrium, a silvery-grey metal, is added to the zirconia during manufacture. This choice is mainly due to availability and cost (70% of the world's supply of zirconia comes from Australia).

YSZ exhibits purely oxygen ionic conduction (with no electronic conduction). The crystalline array of ZrO_2 has two oxide ions to every zirconium ion. But in Y_2O_3 there are only 1.5 oxide ions to every yttrium ion. The result is vacancies in the crystal structure where oxide ions are missing. So, oxide ions from the cathode leap from hole to hole until they reach the anode. The most commonly used stabilising dopants are CaO, MgO, Y_2O_3, Sc_2O_3 and certain rare earth oxides such as Nd_2O_3,

Sm_2O_3, Yb_2O_3.Other oxide based ceramic electrolyte that can be used in SOFCs include:

- Cerium oxide doped with samarium (SDC), $(Ce_{0.85}Sm_{0.15})O_{1.925}$
- Cerium oxide doped with gadolinium (GDC), $(Ce_{0.90}Gd_{0.10})O_{1.95}$
- Cerium oxide doped with yttrium oped Ceria (YDC), $(Ce_{0.85}Y_{0.15})O_{1.925}$
- Cerium doped with calcium (CDC), $(Ce_{0.88}Ca_{0.12})O_{1.88}$
- Lanthanum gallate ceramic that include lanthanum strontium gallium magnesium (LSGM), $(La_{0.80}Sr_{0.20})$ $(Ga_{0.90}Mg_{0.10})O_{2.85}$ or $(La_{0.80}Sr_{0.20})(Ga_{0.80}Mg_{0.20})O_{2.80}$
- Bismuth yttrium oxide (BYO), $(Bi_{0.75}Y_{0.25})_2O_3$
- Barium Cerate (BCN), $(Bi_{0.75}Y_{0.25})_2O_3$ and
- Strontium Cerate (SYC), $Sr(Ce_{0.95}Yb_{0.05})O_3$

Fig. 5 shows, as an example, variation of ionic conductivity with operating temperature for various electrolyte materials [14].

3.5.2. Anode

Metals can be used as SOFC anode materials because of the reducing conditions of the fuel gas. Moreover, these metals must be non-oxidised since the composition of the fuel changes during the operation of the cell. SOFC anodes are fabricated from composite powder mixtures of electrolyte material (YSZ, GDC, or SDC) and nickel oxide NiO (the nickel oxide subsequently being reduced to nickel metal prior to operation) [14], which serves to inhibit sintering of the metal particles and to provide a thermal expansion coefficient comparable to those of the other cell materials.

- NiO/YSZ anode material is suited for applications with YSZ electrolyte material

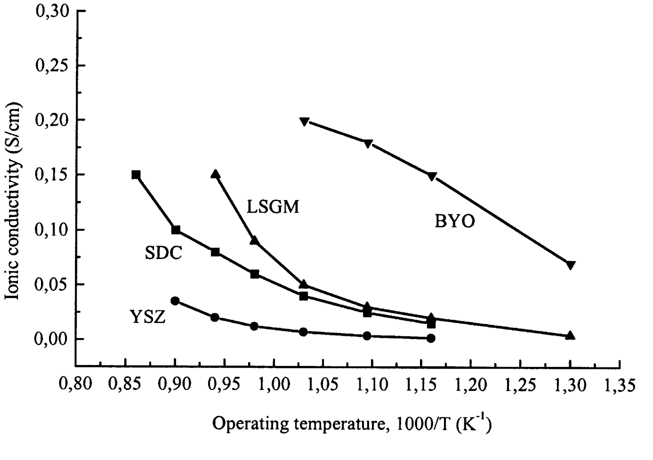


Fig. 5. Typical ionic conductivity of some electrolyte materials as a function of operating temperature [14]

- NiO/SDC and NiO/GDC anode materials are best used with ceria-based electrolyte materials.

The anode structure is fabricated with a porosity of 20–40% to facilitate mass transport of reactant and product gases.

3.5.3. Cathode

Because of the high operating temperature of the SOFC, only noble metals or electronic conducting oxide can be used as cathode materials. Noble metals are unsuitable for practical applications because of their prohibitive cost and insufficient long term stability [13]. Several heterometallic oxides have been proposed and tested. The choice of the electrode material depends on the target application, the specific ceramic electrolyte material, the desired operating temperature range, the electrochemical cell design, and the specific ceramic fabrication methods. The most common applications for these materials are as cathode materials for solid oxide fuel cells and as electrode materials for oxygen generation systems. Perovskite-type lanthanum strontium manganite, $LaSrMnO_3$ (LSM) and lanthanum calcium manganite, $LaCaMnO_3$ (LCM) offer excellent thermal expansion match with zirconia electrolytes and provide good performance at operating temperatures above 800°C. For applications requiring lower temperature operation (600–800°C), a range of alternative perovskite-structured ceramic electrode materials are available. These include:

- Lanthanum strontium ferrite (LSF), $(LaSr)(Fe)O_3$
- Lanthanum strontium cobaltite (LSC), $(LaSr)CoO_3$
- Lanthanum strontium cobaltite ferrite (LSCF), $(LaSr)(CoFe)O_3$
- Lanthanum strontium manganite ferrite (LSMF), $(LaSr)(MnFe)O_3$
- Samarium strontium cobaltite (SSC), $(SmSr)CoO_3$
- Lanthanum calcium cobaltite ferrite (LCCF), $(LaCa)(CoFe)O_3$
- Praseodymium strontium manganite (PSM), $(PrSr)MnO_3$ and
- Praseodymium strontium manganite ferrite (PSMF), $(PrSr)(MnFe)O_3$

For even better electrode performance, some companies offer a line of composite electrode powders, with electrolyte materials (YSZ, SDC or GDC) admixed with the perovskite electrode materials (LSM, LSF, or PSMF). The incorporation of electrolyte material into the cathode material has been shown to improve electrode performance at lower temperatures by increasing the volume of active sites available for electrochemical reactions [14].

Similar to the anode, the cathode is a porous structure that must permit rapid mass transport of reactant and product gases.

3.5.4. Fuel

SOFCs require only a single partial oxidation reformer to pre-process their fuel, which can be gasoline, diesel, natural gas, etc. The nature of the emissions from the fuel cell will vary correspondingly with the fuel mix. Using hydrocarbons, for which a supply infrastructure is currently available, offers a variety of advantages over

using hydrogen. First of all, hydrocarbons are much easier to transport and to store because they are in a stable state which requires no processing before use. They are also more efficient at producing energy. Methane for example yields eight electrons per molecule whereas hydrogen only yields two electrons energy. This advantage could be magnified with the use of more complex hydrocarbons, such as pentane [15].

3.6. Cell geometries and stack configuration

These type of fuel cells come in many forms and can be combined to form a series array of units or stack since most individual fuel cells are small in size and produce between 0.5 and 0.9 volts of DC electricity. One type of SOFC consists of an array of meter-long tubes called tubular configuration which operates with the fuel on the outside surfaces of the bundle of tubes, and the oxidant on the inside, the tube itself being composed of the electrolyte and electrode 'sandwich', as shown in Fig. 6. Other types include a compressed disc that resembles a CD, known also as radial planar design, in which reactant gases do not flow in an open passage along an electrode surface, but diffuse through the porous electrode microstructure from the center to the periphery of the disk (Fig. 7). Planar SOFCs are under development by a number of companies, with Siemens and Fuji Electric two of the leaders. In this case the cells are flat-plates bonded together and placed one on top of the other to form a stack. During operation of the flate-plate, shown in Fig. 8, hydrogen and air flow down channels in the bipolar plates, where on one side each electrode face is exposed to the reactant gases. Oxygen entering the cathode compartment is adsorbed to the cathode, diffuses to the electrode–electrolyte interface and is reduced (i.e. gain of electrons) by the incoming electronic charge. Another variation presents a thin-film configuration design, as illustrated in Fig. 9, for operation at intermediate temperatures. This configuration exploits mature, cost effective electronics-industry-based thin film fabrication processes to integrate bulk fuel cell technology. Completed cells can then be integrated into a manifold that would support the thin film structure, circulate fuel and oxidizer, and collect the generated current [16]. Depending on the cell configuration (tubular or planar), the reactant gases may flow

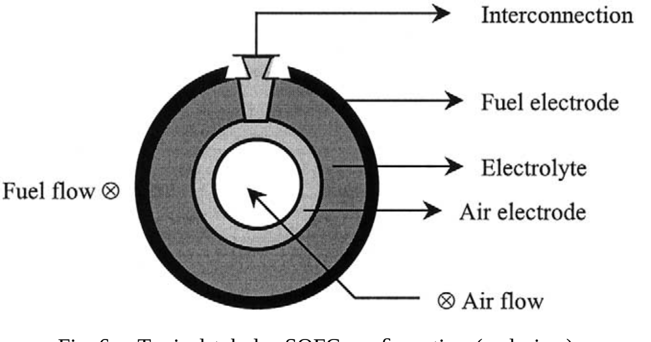


Fig. 6. Typical tubular SOFC configuration (end view).

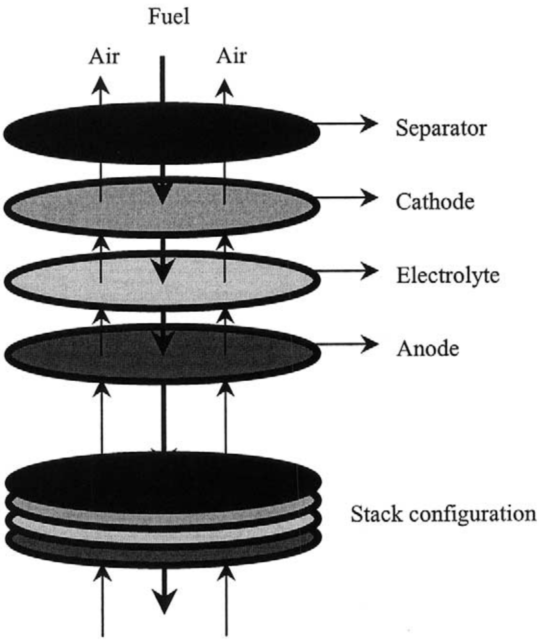


Fig. 7. Typical radial planar SOFC configuration.

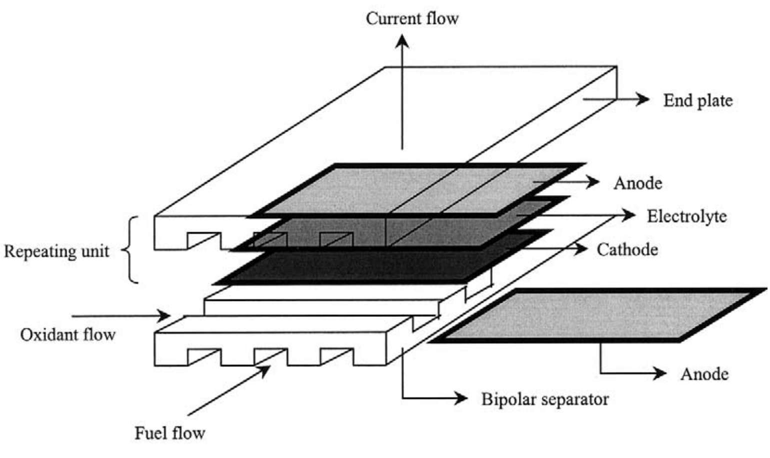


Fig. 8. Typical planar flat-plate SOFC configuration.

in annular, radial, or parallelepiped spaces. However, no matter which design is employed, the fundamental electrochemical processes of cell operation remain the same.

To produce significant amounts of power, practical SOFC elements are assembled into a stack, analogous to a multi-layered sandwich as illustrated in Figs. 7 and 8.

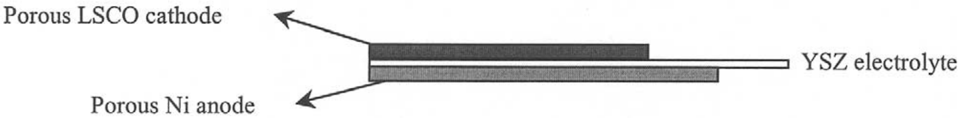


Fig. 9. Typical thin film SOFC configuration.

The stack is the main component of the power section in a fuel cell power plant in which cell assemblies, each including an anode, electrolyte, and cathode, are stacked with interconnecting plates between them that connect the anode of one cell to the cathode of the next cell in the stack. These plates are generally made of doped lanthanum chromite $LaCrO_3$, particularly suitable from its high electronic conductivity, its stability in the fuel cell environment and its compatibility with other cell components. Plates are shaped to allow flow of the hydrogen and oxygen to the repeating unit. Very few oxides can be considered for interconnect applications. Early SOFCs used doped $CoCr_2O_4$ as interconnect material [17]. Recently, $YCrO_3$ compound, having great stability in the fuel cell environment, has been evaluated as an alternative material to $LaCrO_3$ [18]. Glass composite interconnect have also been considered along with $LaCrO_3$ coated metallic interconnect. The coating process is aimed to protect metal from oxidation and corrosion under fuel cell operation conditions. $LaCrO_3$ material performed satisfactory, however, it represents a costly component in the SOFC. The primary concerns regarding low cost interconnect material, such as stainless steel, are a thermal expansion mismatch with other SOFC components and long term instability during cell lifetime. Efforts of scientists are mainly concerned with reducing the SOFC operating temperature which, certainly, will avoid expensive and technologically difficult interconnect material to be used and contribute to lower cost of SOFC systems.

The cells are connected in electrical series to build a desired output voltage and can be configured in series, parallel, series-parallel or as single units, depending upon the type of applications. The number of fuel cells in a stack determines the total voltage, and the surface of each cell gives the total current.

In a SOFC, fuel not consumed by this electrochemical reaction flows through the system and reacts with oxygen from the external environment as soon as it meets it. This generates heat which can be used to keep a stack of SOFC elements at the required temperature.

Although several stack designs are being considered around the world, the most common configuration is the planar (or ‘flat-plate’) SOFC, illustrated in Fig. 8, with its relative ease of manufacture and a lower ohmic resistance of the electrolyte, resulting in reduced energy losses.

4. SOFC benefits and limitations

SOFCs have many advantages: they can be modular, they can be distributed to eliminate the need for transmission lines, they operate quietly and are vibration free.

SOFCs could provide higher system efficiency, higher power density, and simpler designs than fuel cells based on liquid electrolytes. At low enough costs, they could compete with combined cycle gas turbines for distributed applications. The high cell operating temperature enables high reactant activity and therefore facilitates fast electrode kinetics (large exchange currents) and reduced activation polarization. This is especially advantageous as precious platinum electrocatalysts are not required and the electrodes cannot be poisoned by carbon monoxide. As a result, carbon monoxide is a potential fuel in SOFCs. Moreover, the operating temperatures are sufficiently elevated, thereby performance issues are not related to kinetics (activation overpotentials) but to ohmic losses due to charge transport across components and component interfaces [19]. The benefits of SOFCs also include:

- Energy security: reduce oil consumption, cut oil imports, and increase the amount of the country's available electricity supply.
- Reliability: achieves operating times in excess of 90% and power available 99.99% of the time.
- Low operating and maintenance cost: the efficiency of the SOFC system will drastically reduce the energy bill (mass production) and have lower maintenance costs than their alternatives.
- Constant power production: generates power continuously unlike backup generators, diesel engines or Uninterrupted Power Supply (UPS).
- Choice of fuel: allows fuel selection, hydrogen may be extracted from natural gas, propane, butane, methanol and diesel fuel.

Up until now, SOFCs have been most fuel-efficient operating at 1000°C. Unfortunately, this high temperature decreases the cell lifetime and increases the cost of materials, since expensive high temperature alloys are used to house the cell, and expensive ceramics are used for the interconnections, increasing the cost of the fuel cell substantially. Lower operating temperature has been recognised worldwide as the key point for low-cost SOFCs. The reduction in the temperature will therefore allow the use of cheaper interconnecting and structural components, such as stainless steel. A lower temperature will also ensure a greater overall system efficiency and a reduction in the thermal stresses in the active ceramic structures, leading to a longer expected lifetime of the system and make possible the use of cheaper interconnect materials such as ferritic steels, without $LaCrO_3$ protective coatings, as already mentioned. For some years, scientists and researchers throughout the world have been on a quest to drop the operating temperature of SOFCs without sacrificing their performance.

The 600–1000°C operating temperature of the SOFC requires a significant start-up time. The cell performance is very sensitive to operating temperature. A 10% drop in temperature results in ~12% drop in cell performance, due to the increase in internal resistance to the flow of oxygen ions [20]. The high temperature also demands that the system include significant thermal shielding to protect personnel and to retain heat.

5. SOFCs and their environmental impact

Issues of efficiency and ecology converge at this time to renew interest in SOFCs as systems for electricity generation. In recent times, they attract serious attention in the utility industries, particularly in co-generation of heat and power. The environmental impact of SOFC use depends upon the source of hydrogen-rich fuel used. If pure hydrogen is used, fuel cells have virtually no emissions except water and heat. As mentioned earlier, hydrogen is rarely used, due to problems with storage and transportation, but in the future many people have predicted the growth of a solar hydrogen economy. In this scenario, photovoltaic cells would convert sunlight into electricity. This electricity would be used to split water (electrolysis) into hydrogen and oxygen, in order to store the sun's energy as hydrogen fuel [21]. In this scenario, SOFCs generating stations would have no real emissions of greenhouse or acid gases, or any other pollutants.

It is predominantly during the fuel processing stage that atmospheric emissions are released by a fuel cell power plant. However, the high efficiency of SOFC results in less fuel being consumed to produce a given amount of electricity, which corresponds to a lower emission of carbon dioxide CO_2, the main 'greenhouse gas' responsible for global warming. When hydrogen from natural gas is used as a fuel, SOFCs have no net emissions of CO_2 because any carbon released is taken from the atmosphere by photosynthetic plants. A reduction of carbon dioxide emissions by more than 2 million kg per year can be obtained. Moreover, emissions from SOFC systems will be very low with near-zero levels of NO_x, SO_x and particulates, therefore eliminates 20,000 kg of acid rain and smog-causing pollutants from the environment. In any case SOFCs generally provide the lowest emissions of any non-renewable power generation method such as traditional thermal power plants, as shown in Table 6 [9]. This is very important with regard for energy related environment concerns. When combined with a heat engine that uses any waste heat, SOFCs are the most clean and efficient devices available for this purpose.

SOFC can also provide high-quality waste heat that can be used to warm the home or provide refrigeration and air conditioning without harming the environment. Armstrong says: "Its only emissions are steam, trace amounts of nitrogen oxides and sulfur oxides, and a small amount of carbon dioxide."

If CO_2 can be removed at the source for disposal elsewhere, the SOFC really would become the ultra-high efficiency, zero emissions power plant of the 21st cen-

Table 6
Typical SOFC air emissions from one year of operation [9]

Air emissions[a]	SO_X	NO_X	CO	Particles	Organic compounds	CO_2
Fossil fuelled plant	12,740	18,850	12,797	228	213	1,840,020
SOFC system	0	0	32	0	0	846,300

[a] kgs of emissions per 1650 MWh from one year full operation

tury. A particular interest on SOFCs related concepts can be dated in April 1999 by an intiative of NEDO international joint research programme. The main objective of this joint international research team (J. A. Kilner from Imperial College of Science in UK, T. Ishihara from Oita University in Japan, K. Otsuka from Tokyo Institute of Technology in Japan, J. T. S. Irvine from the University of St Andrews in UK, and J. Yi from the Dalian Institute of Chemical Physics in China) is to study the fundamentals of oxide ion transport phenomena in perovskite structured mixed oxides, suitable for use as the cathode, anode and electrolyte of an all-perovskite SOFC and capable of operating at reduced temperatures 500–600°C. The aim of the program is to demonstrate a zero emission demonstrator unit by the end of the three-year period, and open new research frontiers of an environmentally-friendly energy production system.

6. Applications of SOFCs

Combined with low noise and ability to utilize readily-available fuel such as methane and natural gas, SOFC generators are best suited for the provision of power in utility applications, due to the significant time required to reach operating temperatures, and can have broad applications ranging from large-scale power plants to smaller home-scale power plants and portable/emergency power generators. SOFCs could be used in many applications. Each proposed use raises its own issues and challenges. Their most needed uses are:

- High power reliability: computer facilities, call centres, communication facilities, data processing centres high technology manufacturing facilities.
- Emission minimisation or elimination: urban areas, industrial facilities, airports, zones with strict emissions standards.
- Limited access to utility grid: rural or remote areas, maximum grid capacity.
- Biological waste gases are available: waste treatment plants, SOFC can convert waste gases (methanol from biomass) to electricity and heat with minimal environment intrusion.

7. Future of SOFCs

Focusing their efforts on SOFCs, which have been on the verge of commercial viability for years, researchers around the world are making a concerted effort in the development of suitable materials and the fabrication of ceramic structures which are presently the key technical challenges facing SOFCs. Programs are underway in Japan and in the US that use a relatively simple ceramic process to develop a thin-film electrolyte that decreases the cell resistance, and both doubles the power output and significantly reduces the cost of SOFCs. There is also a current effort in integrating the SOFCs and developing a novel stacking geometry. The demonstration of low-temperature SOFC operation directly on methane, signals an important new

opportunity for making simple, cost-effective power plants [22]. The global SOFC making company continues to realize very significant improvements in basic fuel cell design. A measure of their success is the realisation of a 48.6% improvement in single cell power densities (see Table 7) which represents the highest published power densities for commercial-sized SOFCs in the world [22]. Changes in cell composition and design have resulted in these improved power densities. Higher power densities contribute to lower weight, size and cost of fuel cell systems.

SOFCs could someday be suitable for small-scale residential market applications if ultimate cost goals of $1000/kW are reached. An estimate of materials costs made by MSRI (Material Science and Research Incorporation) in Salt Lake City is shown in Table 8 [23]. Table 9 shows the California energy commission mid-term goals in the application of SOFCs, for the period 2005–2010 with a willing power density target of 300 mW/cm^2 and an installed capacity of 50,000 units/year [24].

8. Conclusion

Energy exploitation of fossil fuels is reaching its limits. Future alternatives must therefore be developed for long-term and environmental-friendly energy supply needed by a constantly growing world population. SOFCs provide highly efficient, pollution free power generation. Their performance has been confirmed by successful operation power generation systems throughout the world. Electrical-generation efficiencies of 70% are possible nowadays, along with a heat recovery possibility. SOFCs appear to be an important technology for the future as they operate at high efficiencies and can run on a variety of fuels, from solar hydrogen to methanol, from biomass to gassified coal. As the technology develops, and if the cost of fossil fuels continues to rise, this clean, efficient alternative will stimulate the thermomechanical engineers, despite their Carnot and Rankine limitations, to even greater efforts for the SOFCs to find more and more practical uses. The United Nations agency GEF (Global Environment Facility), which operates through The UN Development and Environment Programs and the World Bank, is launching a fuel cell projects of more than $130 million between 2002 and 2003 for major cities and capitals with some of the world's worst air pollution levels in Brazil, Mexico, Egypt, India and China

Table 7
Evolution of single SOFC performance measured in Watts/cm^2 at 0.7 V using H_2 as fuel [22]

Type & Year	Temperatures 600°C	650°C	700°C	750°C	800°C
G1-1998	–	–	–	0.150	0.250
G2-1999	0.156	0.318	0.487	0.528	0.594
G3-2000	0.197	0.382	0.635	0.900	1.093
G4-2000	0.200	0.416	0.723	1.093	1.216

Table 8
Materials cost per kilowatt [23]

Component	Material	Cost/kg ($)	Thickness (μm)	Weight (g)	Total cost[a] ($) per kW & component
Electrolyte	YSZ	10	10	12	0.12
Anode	Ni+YSZ	15	1500	1365	20.50
Cathode	LSM	25	100	60	1.50
Interconnect	Metallic alloy	15	125	200	3.00
Total				1631	25.12

[a] costs estimate are based on 0.5 W/cm^2 at an operating temperature of 800°C

Table 9
Desired performance targets and stretch goals for SOFC systems [24]

Parameter	Target	Stretch goal	Notes
Capital cost, installed ($/kW)	800	400	2005–2010 at 50,000 units/year
Power degradation	<1% per 1000 hr	<0.5% per 1000 hr	For year 2005-2010
Power density (mW/cm^2)	300	500	>4 cell stack and>25 cm^2 electrode

[25]. The basic of GEF strategy is to use relatively modest incremental financing to steer industry resources to the need of developing countries for clean technologies, and their studies indicate that greenhouse gas stabilisation can be achieved only through early investments in new technologies, because the returns are potentially larger. A new report unveiled recently by J. Barrett of the US Economic Policy Institute (EPI) and J. A. Hoerner of the Center for a Sustainable Economy (CSE), suggests that global warming can be reduced without harming the economy and that nobody needs to accept a choice between environmental degradation and economic calamity.

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